



PCT/SG 2004/000358

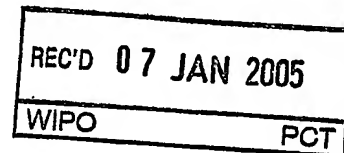
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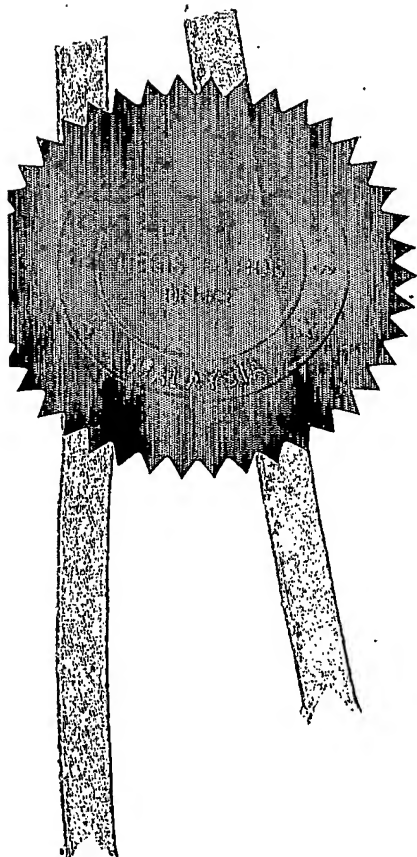
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**PATENT APPLICATION NO: PI 2003 4288**

This is to certify that annexed hereto is a true copy from the records of the Registry of Trade Marks and Patents, Malaysia of the application as originally filed which is identified therein.



By authority of the  
REGISTRAR OF PATENTS

**ROZANAH MISKAN**  
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**CERTIFICATE OF FILING**

**APPLICANT** : 1) UNIVERSITI TEKNOLOGI MALAYSIA  
2) PINTAS PTE LTD  
**APPLICATION NO** : PI 20034288  
**REQUEST RECEIVED ON** : 10/11/2003  
**FILING DATE** : 10/11/2003  
**AGENT'S/APPLICANT'S FILE REF.** : PIP/0748/UTM/03/LCH/SOH

Please find attached, a copy of the Request Form relating to the above application, with the filing date and application number marked thereon in accordance with Regulation 25(1).

**Date** : 20/12/2004

  
.....  
**(NOOR MOHAMAD HAZMAN B. HAMID)**

**For Registrar of Patents**  
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Patents Form No. 1  
PATENTS ACT 1983

REQUEST FOR GRANT OF PATENT  
[Regulations 7 (1)]

To: The Registrar of Patents  
Patent Registration Office,  
Kuala Lumpur, Malaysia

For Official Use  
APPLICATION NO : **PI 20534288**  
Application received on : **10-11-2003**

Fee received on : **10-11-2003**

Amount : **RM230**

\* Cheque/Postal Order/Money Order/Draft/Cash  
No.: **OLB 148152**

Please submit this Form in duplicate  
together with the prescribed fee.

Applicant's or Agent's file reference

**PIP/0748/UTM/03/LCH/Soh**

THE APPLICANT (S) REQUEST (S) THE GRANT OF A PATENT IN RESPECT OF THE  
FOLLOWING PARTICULARS:

I. Title of Invention: **Improvements in Silica Aerogels**

II. APPLICATION(S) *(the data concerning each applicant must appear in this box or,  
if the space is insufficient, in the space below):*

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Additional Information (if any)

10 NOV 2003

III.

INVENTOR(S):

Applicant is the inventor(s):

Yes

☐

No

☒

Name of inventor

Address:

**Halimatun Hamdan**

**Ibnu Sina Institute for Fundamental  
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Malaysia.**

A statement justifying the applicant's right to the patent accompanies this Form:

Yes

☒

No

☐

Additional Information (if any)

IV.

AGENT OR REPRESENTATIVE:

Applicant(s) has appointed a patent agent in accompanying Form No. 17  
(will follow)

Yes

☒

No

☐

Agent's Registration No:

**PA/99/0077**

Applicants have appointed:

**LOK CHOON HONG**

to be their common representative.

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V. DIVISIONAL APPLICATION:

This application is a divisional application ☐  
The benefit of the filing date ☐ priority date ☐ of the initial application  
is claimed in as much as the subject-matter of the present application is contained  
in the initial application identified below:

Initial Application No.: .....

Date of filing of initial application: .....

VI. DISCLOSURES TO BE DISREGARDED FOR PRIOR ART PURPOSE:

Additional information is contained in supplemental box:

(a) Disclosure was due to acts of applicant or his predecessor in title ☐  
Date of disclosure: .....

(b) Disclosure was due to abuse of rights of applicant or his predecessor in title ☐  
Date of disclosure: .....

A statement specifying in more detail the facts  
concerning the disclosure accompanies this Form

Yes ☐

No ☒

Additional Information (if any)

VII. PRIORITY CLAIM (if any):

The priority of an earlier application is claimed as follows:

Country

Filing Date

Application No.

Symbol of the international Patent Classification:  
If not yet allocated, please tick

☐

The priority of more than one earlier application is claimed:

☐

The certified copy of the earlier application (s) will furnished  
by the patent agent upon request

☐

Additional Information (if any)

## VIII

## CHECK LIST

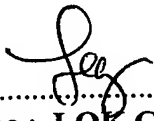
A. This application contains the following:

1. Request (Form 1)	4	sheets
2. description	7	sheets
3. claim	2	sheets
4. abstract	1	sheets
5. drawings	<u>0</u>	sheet
Total	14	sheets

B. This Form, as filed, is accompanied by the items checked below:

- (a) signed Form No. 17 (will follow) ☒
- (b) declaration that inventor does not wish to be named in the patent ☐
- (c) statement justifying applicant's right to the patent, ☒
- (d) statement that certain disclosures be disregarded ☐
- (e) priority document(certified copy of earlier application) ☐
- (f) cheque ☒
- (g) other documents (specify) ☐

## IX. SIGNATURE

  
 Name : **LOK CHOON HONG**  
 Agent's Registration No.: **PA/99/0077**

10 Nov 2003  
 Date

## For Official Use

1. Date application received:.....
2. Date of receipt of correction, later filed papers or drawings completing the application :  
 .....

\* Delete whichever does not apply.

\*\* Type name under signature. Pursuant to regulation 24, a declaration of withdrawal must be signed by the applicant (s) or by the agent so authorized for that specific purpose.

10 NOV 2003

20034282

## Improvements in Silica Aerogels

### Field of Invention

This invention relates to silica aerogels and to a method for their preparation.

5

### Background of the Invention

An aerogel is a gel in which the liquid phase has been replaced by air without damaging the solid phase leaving a lattice structure of substantially the same shape as the gel and of only slightly reduced volume. Silica aerogels have a lattice structure formed of  
10 amorphous silica ( $\text{SiO}_2$ ).

Silica aerogels are extremely light materials, having a specific gravity as low as  $0.025\text{g/cm}^3$ , the lowest thermal conductivity of any known solid material, high surface area and high porosity. This makes them very suitable for use in many applications. Very  
15 low specific gravity aerogels have been used, for example in aerospace applications as insulating materials on space craft, and particularly on the rover vehicle for the Mars Pathfinder project and as Cerenkov detectors for capturing high velocity cosmic particles, which can easily penetrate the porous material, where they are gradually decelerated to achieve a "soft landing". The particles trapped in transparent aerogels can even be  
20 inspected *in situ*. They have been used as catalysts and catalyst supports, where their surface area and porosity makes them especially useful, and in insulation and heat storage systems. There are many instances where aerogels could be used or used to a greater extent were their cost not so high. The cost of aerogels, at present, is high both because of their cost of preparation and the cost of the starting materials.

25

The first commercially produced aerogels were made by a process that comprises adding sulphuric acid to a solution of sodium silicate with the 30 concentrations being controlled to form a gel having 9 % silica content. After the gel has aged for several hours to allow it to strengthen, due to syneresis phenomena, it is passed through a roll crusher into a  
30 wash tank where water is passed over the gel to remove the sodium sulphate formed in the gel preparation reaction. When the gel has been sufficiently washed, all excess water

is removed by draining and the gel is then covered with alcohol to replace the water in the gel with alcohol. After a suitable soaking time the alcohol is drained off and replaced with fresh alcohol. This alcohol washing procedure is repeated several times.

- 5 When the water in the gel has been substantially replaced with alcohol, the excess alcohol is drained off and the gel charged to an autoclave, in which it is slowly heated to a temperature above the critical temperature of the alcohol with the pressure being maintained at a level above the critical pressure of the alcohol. When the temperature reaches the desired level, the pressure is reduced to atmospheric and the autoclave is  
10 finally evacuated to a level slightly below atmospheric for a short period.

The success of this process is based on one essential step, namely, the heating of a gel system to temperatures and pressures above the critical temperatures and pressures of the liquid phase of the gel, which allows the liquid phase to be removed without destroying  
15 the lattice structure of the gel with consequent formation of a dense xerogel rather than a lightweight aerogel.

This process, while it uses fairly cheap reactants, is extremely time consuming because of the need for the washing and multiple solvent exchange steps.

20

In attempts to quicken the process it was subsequently found that silica aerogels could be produced using tetramethyl orthosilicate (TMOS) as starting material. In this method of operation TMOS is hydrolysed with water in the presence of an acidic or basic catalyst, usually in ethanol. After formation of a silica gel by aging and removal of all remaining  
25 water by displacement with alcohol, the gel is dried, as previously, using a super-critical drying technique.

30

Since TMOS is a dangerous material to use because of its toxicity, its use has now been superseded by tetraethyl and other tetraalkyl orthosilicates that are much safer to use.

Tetraalkyl orthosilicates are however very expensive products and hence the silica aerogels produced from them are similarly expensive and their use is limited to high technology applications. If silica aerogels could be manufactured more cheaply their range of application could be far wider.

5

The main drawback of the high temperature variants are the severe temperature conditions, causing accelerated aging of the solution-sol-gel samples. It has been proposed to replace the alcohol in the gel with carbon dioxide, which has a very much lower critical temperature than the alcohols generally used, by flushing the vessel and the  
10 gel with liquid carbon prior to carrying out the critical drying process.

### Summary of the Invention

Rice husk is a plentiful waste material in all rice growing areas. It is primarily disposed  
15 of by open burning, which is, of course, ecologically undesirable, although a small percentage has been used for a variety of purposes. Although rice husk is very rich in silica, and its ash can contain up to 96% of silica, to-date this characteristic has not been exploited to any major extent. The silica from rice ash husk is in a very active form and has been found to be a very useful starting material for silica aerogels.

20

Accordingly, this invention provides a method for producing silica aerogels by a sodium silicate route, wherein rice husk ash is used as the source of silica. The rice husk ash is prepared by burning the rice husk on a heating plate with excess air until the white ash is obtained.

25

According to the invention a silica aerogel is produced by dissolving rice husk ash in aqueous sodium hydroxide, preferably at an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of between 1:3 and 1:4, more preferably about 1:3.33, to produce a sodium silicate solution preferably containing from 1 to 16% by weight of  $\text{SiO}_2$ , adding concentrated sulphuric acid to the resulting  
30 water glass solution to convert the sodium silicate to silica and produce a silica hydrogel, aging the hydrogel to allow the gel structure to develop, preferably for a period of up to

40 days, displacing the water with a  $C_1$  to  $C_4$  alcohol, preferably methanol or ethanol, to produce an alcogel, and subjecting the alcogel, optionally after replacing the alcohol by carbon dioxide, to super critical drying to form an aerogel.

- 5 The method of the invention allows the preparation of mesoporous aerogels having an average pore diameter of between 2 and 50 nm, usually about 20 nm, and a BET surface area of between 600 and 800  $m^2g^{-1}$ . Their specific gravity lies between 0.03 and 0.07  $g/cm^3$  with the pores accounting for up to 97% of their total volume. Because of this large volume of very small pores they have a low thermal conductivity of between 0.09 and 0.1  $Wm^{-1}K^{-1}$ . These values are comparable to those of aerogels made using tetraethyl  
 10 orthosilicate as starting material but the aerogels are very much cheaper to produce because of the cheaper starting materials.

- The water is preferably displaced from the hydrogel using a Soxhlet extraction technique  
 15 by suspending the sample in the vapour above boiling alcohol in a reflux system while allowing the displaced water to escape.

- The super-critical extraction is preferably carried out by placing the alcogel with additional alcohol in an autoclave fitted with a thermocouple and a temperature controller  
 20 and slowly raising the temperature in the autoclave until the critical temperature and pressure are reached. After a holding time the alcohol vapour is vented by slowly reducing the pressure in the autoclave to atmospheric pressure by a controlled leak and then the temperature is slowly reduced to room temperature. The temperature in the autoclave may be increased, for example at a rate of 50°C/hr for the time necessary to  
 25 reach the critical temperature and the alcohol vented over a period of one and one half hours. The temperature may be reduced over a period of, for example 12 hours. The amount of additional alcohol should be such that there is sufficient alcohol in the autoclave that the critical pressure is reached but the amount above this amount is only limited by safety requirements.

The aerogels obtained are hydrophilic, having hydroxyl groups on their surface, but can be converted to a hydrophobic form by replacing the hydroxyl groups with alkoxy groups. This may be achieved, for example by passing methanol vapour over a heated sample of the aerogel. The methylation reaction is preferably carried out in a closed  
 5 system in which the sample is placed in a tube enclosed in an external furnace and extending between a flask containing boiling methanol and a condenser, which is connected back to the flask. The temperature of the furnace may be of the order of 250°C. The samples are preferably out-gassed at a temperature of about 100°C under a reduced pressure of about  $10^{-5}$  Torr for at least 15 hours both before and after the methylation  
 10 process.

### Detailed Description of the Preferred Embodiments

The following Example illustrates the invention:

15

Rice husk as obtained from the paddy field was washed and dried in open air. The rice husk was then burned on a heating plate at a temperature in the range of 650°C to 700°C with excess air until the white ash was obtained. Preferably the combustion temperature is 700°C due to the rice husk silica burned at this temperature is amorphous to X-Ray  
 20 Diffraction (XRD) and contains up to 92 – 97% of silica with a traces amount of cations. XRD is a high-resolution diffraction instrument for structural studies to investigate the atomic scale structure of condensed matter (i.e. crystalline solids, glasses, liquids, powders, mixtures, etc.). Combustion at 700°C produces the most reactive silica source which predominantly contains pure amorphous  $\text{SiO}_4$  tetrahedra and no SiOH groups as  
 25 found in large amount in the amorphous sample. The presence of SiOH groups and crystalline phase in the silica source reduces the reactivity of the silica. 0.7g of rice husk ash can be produced from 5g of rice husk combustion which contains up to 92 – 97% silica. The purity of silica of above 98% can be achieved by washing the rice husk in 1M sulphuric acid solution, followed by air drying prior to combustion. Samples were  
 30 collected from the center of the ashes and from the fringe. Since silica from rice husk can

be prepared under controlled temperature without any chemical treatment, it is a potential source of highly active amorphous silica.

38 grams of the rice husk ash, which contained about 95% silica was dissolved in 14  
5 grams of sodium hydroxide pellets in 450 ml water and stored, with stirring at 90°C in a PTFE bottle to produce a sodium silicate solution having a silica content of 8% by weight and a ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  of 1:3.33. 100-150 grams of 96% sulphuric acid was then added to 200g of sodium silicate solution to form a hydrogel. Hydrogels from the two samples  
10 of rice husk ash were aged at 25°C for periods ranging from 1 to 5 days. The hydrogels were thoroughly washed with water to remove the sodium sulphate formed in the conversion from sodium silicate to silica.

Samples of the various aged hydrogels were transferred to cloth bags and converted to alcogels by replacing their water with ethanol by suspending a bag containing a sample  
15 in a Soxhlet column fitted with a water-cooled reflux condenser above a flask of boiling ethanol and subjecting the sample to the alcohol vapour for a period of 16 hours.

The alcogels resulting from the ethanol extraction were then subjected to supercritical drying in a 2 litre Parr autoclave. 260 cm<sup>3</sup> of the alcogel was placed in the autoclave with  
20 500 ml additional ethanol and after sealing the autoclave the temperature was raised to 275°C over a period of 7 hours at a rate of 50°/hour to 200°C and thereafter at 25°C/hour. The temperature was maintained at 275°C for one hour and the ethanol vapour was then allowed to bleed from the autoclave at such rate that the pressure fell to atmospheric over a period of one and a half hours. The temperature in the autoclave was then reduced to  
25 room temperature at a steady rate.

The properties of the various aerogels obtained are listed in the following table.

## Physical Properties of silica aerogel

	Property	Aerogels of Example	Commercial aerogel
5	Apparent density	0.03-0.06g/cm <sup>3</sup>	0.1 g/cm <sup>3</sup>
	Internal Surface Area	700-900 m <sup>2</sup> /g	600-1000 m <sup>2</sup> /g
	Mean Pore Diameter	20.8 nm	20 nm
	Particle Diameter	5 nm	2-5 nm
	Thermal Tolerance	to 500 C, mp >1200 C	to 500C, mp > 1200 C
10	Thermal Conductivity	0.099 Wm <sup>-1</sup> K <sup>-1</sup>	0.089 Wm <sup>-1</sup> K <sup>-1</sup>

### Claims

1. A method for producing a silica aerogel, which comprises combustion of rice husk until the white ash is obtained, dissolving rice husk ash in aqueous sodium hydroxide, heating and stirring the resultant gel mixture to produce a sodium silicate solution, adding concentrated sulphuric acid to the resulting water glass solution to convert the sodium silicate to silica and produce a silica hydrogel, aging the hydrogel to allow the gel structure to develop, displacing the water with a C<sub>1</sub> to C<sub>4</sub> alcohol, to produce an alcogel, and subjecting the alcogel, to super critical drying to form an aerogel.
2. The method according to Claim 1 wherein the rice husk is combusted at a temperature in the range of 600°C to 700°C with excess air until the white ash is obtained.
3. The method according to Claims 1 to 2, wherein the rice husk ash contains 92 – 97% of amorphous silica and trace amount of cations.
4. The method according to Claim 3, wherein trace amount of cations present in rice husk silica are K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>.
5. The method according to Claims 1 to 4, wherein the purity of silica of above 98% can be achieved by washing the rice husk in 1M sulphuric acid solution, followed by air drying prior to combustion.
6. The method according to Claim 1, wherein the amounts of rice husk ash and sodium hydroxide are such as to give a ratio of Na<sub>2</sub>O:SiO<sub>2</sub> of between 1:3 and 1:4.
7. The method according to Claim 1, wherein the ratio of Na<sub>2</sub>O:SiO<sub>2</sub> is about 1:3.33.

8. The method according to Claim 1 to 7, wherein the sodium silicate solution contains from 8 to 10% by weight of  $\text{SiO}_2$ .
- 5 9. The method according to Claim 8, wherein the sodium silicate solution contains 9% by weight of  $\text{SiO}_2$ .
10. The method according to any one of Claims 1 to 9, wherein the hydrogel is aged for a period of up to 5 days.
- 10 11. The method according to Claims 1 to 10, wherein the  $\text{C}_1$  to  $\text{C}_4$  alcohol is methanol or ethanol.
12. The method according to any one of Claims 1 to 11, wherein hydrophilic aerogels are converted to hydrophobic aerogels by alkylation.
- 15 13. Silica aerogels produced by a process according to any one of claims 1 to 12.

**Abstract****Improvements in Silica Aerogels**

- 5 This invention relates to silica aerogels and to a method for their preparation from rice husk. Rice husk is very rich in silica, and its ash can contain up to 92-97% of amorphous silica. The rice husk ash is prepared by burning the rice husk on a heating plate with excess air until the white ash is obtained. Silica from rice ash husk is in a very active form and has been found to be a very potential starting material for silica aerogels.

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